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An extension of the time–temperature superposition principle to non-linear viscoelastic solids

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Abstract

An experimental data treatment is introduced to manage with the tensile test responses of highly non-linear viscoelastic solids such as solid propellants. This treatment allows the representation of a set of strain–stress curves by a single intrinsic non-linear response which is found independent of the experimental conditions of rate and temperature. To obtain this result, two independent normalization factors are applied both on the stress and strain axis. The requirement of a normalization factor applied to the strain measure produces a pseudo-strain which is found to be viscoelastic in nature. It is believed that the existence of such a viscoelastic strain measure is the characteristic feature of non-linear viscoelasticity. To confer some generality to the principle, the validity is also checked for volumetric and multiaxial stress response of solid propellant. To illustrate the potential application of the principle, it is applied to build up an idealized material database upon which numerical identification of constitutive non-linear models can be easily performed. Finally, generalization is extended to other filled elastomers such as a carbon black filled SBR.

Keywords: Solid propellants; Mechanical behavior; Non-linear viscoelasticity; Filled elastomers

1. Introduction

Supported by the increasing power of the available numerical tools, the past decade has seen a tremendous development of non-linear viscoelastic models to describe the mechanical behavior of particle filled elastomers. These models have proved to be efficient in numbers of industrial applications ranging from tires conception to solid rocket propellant grains mechanical analysis. However, if a considerable literature addresses the theoretical and numerical aspects regarding these models, very few deal with the difficult path which has to be followed from the collection of the experimental observations to the identification of the model constants. The aim of this work is to propose an original method, based on the accumulated knowledge of solid propellants mechanical behavior, to build up from experimental data, an idealized set of data to input the models identification process. As a definitive advantage, the method provides a set of data points from which the experimental scatter is relieved. The coherence between responses for various strain fields is imposed by simple

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assumptions and the identification allows extrapolation beyond the fracture point. The method consists in a superposition process which allows the identification of a unique intrinsic curve from the measured non-linear mechanical behavior in a wide domain of experimental conditions. Since this unique curve is understood as a material property, the superposition technique may be regarded as an extension of the time–temperature equivalence principle into the field of non-linear material behavior. The validity of the results is demonstrated for the uniaxial tensile response of solid propellants at various rates and temperatures, it is also established for the associated volumetric behavior and for the equibiaxial tensile response. A preliminary result for an SBR industrial rubber foresees the possible generalization of the principle to a wide variety of elastomers.

2. Experimental

2.1. Solid propellants mechanical behavior

2.1.1. Elastic response

Though solid propellants are regarded as filled elastomers, the nature of their structure is more a compact granulate of energetic crystalline particles which may be different in size, in shape and in chemical nature. In this agglomerate, the small volume left between adjacent particles is filled with a synthetic elastomer which represents only a few percent of the overall volume. Despite this complex structure, and since the polymeric phase is soft, the overall mechanical behavior of the system is controlled by this component. As a consequence, the elastic response description refers generally to the entropic elasticity theory and hyperelastic models.

2.1.2. Volumetric behavior

In opposition to common carbon black filled rubbers, for propellants, the selection of both the crystalline particles and the synthetic elastomers is not dictated by the optimization of the mechanical resistance. Obviously, the optimum choice of these ingredients has to enhance the energetic performance rather than the mechanical properties. These properties are then a result of the formulation adjustments and are expected to match the structure integrity requirements with very few means of improvement. Among these means, and regarding the fact that the main failure mechanism in these materials is the debonding process occurring between the binder and the particles, the adhesion quality is of a crucial importance. A convenient test device to measure the resistance of a particular propellant composition with respect to debonding is the Farris (1968) gas dilatometer which allows for the simultaneous recording of the volume dilatation during a conventional uniaxial tensile test. Fig. 1 depicts the device principle together with a typical result for an HTPB/AP (Ammonium Perchlorate) solid propellant.

The response is analyzed as the succession of three distinct domains each one corresponding to different states of the material structure degradation. At moderate deformations, the material is incompressible and the volume remains constant. Beyond a certain critical level, the particles-binder dewetting process begins and the volume rate increases rapidly with the number of locations where debonding takes place. Once the potential number of particles liable to be debonded is reached, the macroscopic volume increases proportionally with the volume of each single vacuole and the response is linear. As a result of this progressive failure mechanism, the stress response goes from a linear to a highly non-linear regime before the fracture of the sample occurs after a roughly constant stress plateau. The viscoelastic effects, which arise both from the binder bulk behavior and from the intense frictions between particles and binder during the debonding process, strongly affect the volumetric as well as the stress responses. It is still uncertain to settle whether the volume of each vacuole increases with decreasing temperature or if the number of affected sites increases. Whatever it is, the experimental observation shows that considering a given deformation level, an increasing volume is recorded when the experimental conditions approach the material glass transition (low temperatures or high strain rates). It should be reminded that Farris has established (Farris, 1968) the existence of a correlation between the stress response and the second derivative of the volume dilatation versus strain.

2.1.3. Dynamic mechanical analysis

It is convenient to quantify the viscoelastic effects range in a polymer material by dynamic mechanical analysis (DMA). In this technique, the material response is measured during a frequency sweep for different

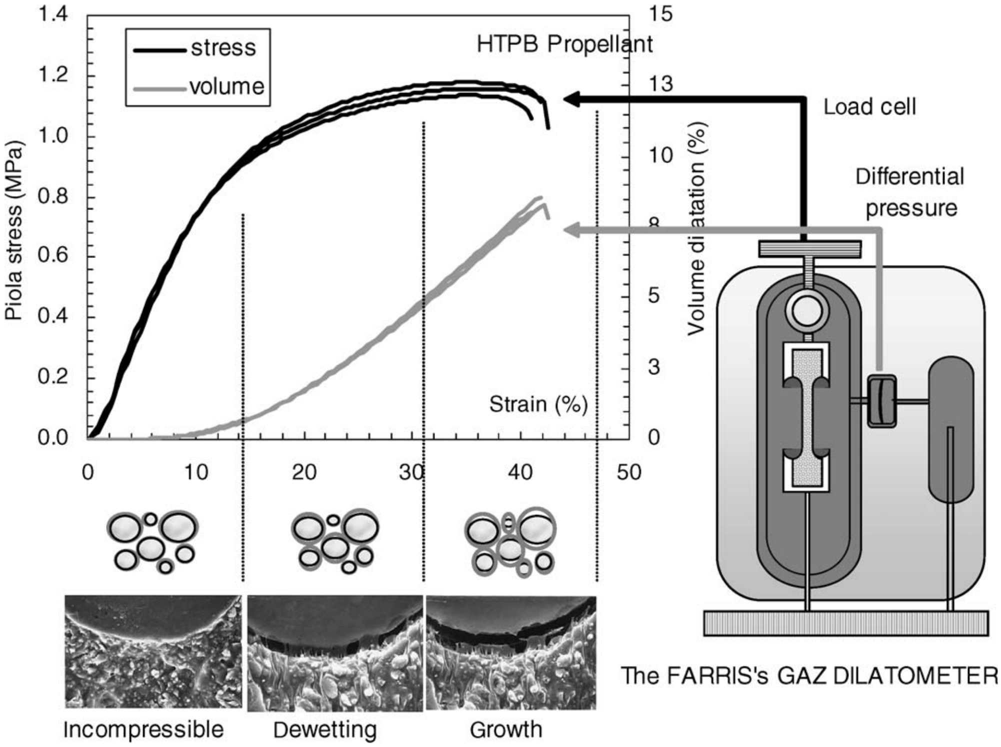

Fig. 1. Volume dilatation response of a solid propellant (Ambient temperature-rate = 8.23 s^{-1}).

isothermal temperatures. From the relative displacement along the frequency axis of the isothermal results, the master curve of the storage modulus may be built up and the shift factors, $\log(a_T)$, derived. These factors represent the amplification in the rate of the macromolecular movements by temperature and equivalently by frequency. These temperature dependent constants are expected to be material properties. Fig. 2 presents for the same HTPB composition of Fig. 1, the master curve construction of the storage modulus and corresponding shift factors.

The shift factors identified will be then used as inputs in the master curves construction of all material properties. For sake of convenience, a temperature dependence adjustment of the shift factors is required:

$$\log(a_T) = (T - T_{réf}) \cdot \{a_2(T - T_{réf})^2 + a_1(T - T_{réf}) + a_0\} \tag{1}$$

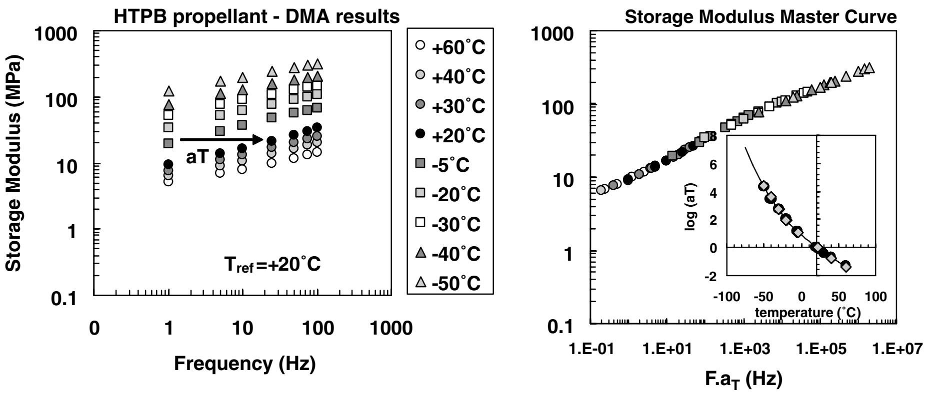

Fig. 2. Master curve construction of the storage modulus.

where $T_{\text{réf}}$ is the reference temperature and the a_i are constants with no physical signification. The master curve construction principle establishes the fact that the modulus observed at a current frequency and temperature will be the same at the reference temperature for a shifted frequency by the corresponding factor $\log(a_T)$. This well verified principle is a powerful method to extend the frequency domain accessible to the experimental observations into a broader frequency domain where the industrial application characteristic times generally lie (for solid propellant rocket motors, these times are the storage duration and the firing time).

2.1.4. Uniaxial tensile behavior

Most of the information required to perform the structural stress analysis of the solid rocket motor grains comes from a set of uniaxial tensile experiments. These experiments are conducted in reference to the JANNAF standard on a conventional screw driven dynamometer for different constant crosshead rates (ranging from 5 to 500 mm/min) and isothermal temperatures conditions ranging from the crosslinking temperature (∼+60 °C) down to the glass transition temperature (∼−70 °C). Considering the sample geometry, the accessible strain rates are limited on the upper bound by the inertia of the machine and on the lower bound by the patience of the experimentalist. The JANNAF sample dimensions, its deformation mode and a typical result for a constant strain rate and different isothermal temperatures of testing are shown in Fig. 3 for an HTPB propellant.

From these tests results, the conventional tensile properties, which are the tensile modulus, E_{tg}, the maximum stress, S_{m}, and the strain at maximum stress, e_{m}, are extracted and plotted in Fig. 4 as master curves using the predetermined shift factors from DMA.

From this database, a viscoelastic kinetics may be adjusted on each property master curve, $P_i(t/a_T)$, using a multiple power law dependence of the reduced time as suggested by Alary to reproduce the observed linear evolution by parts:

$$P(t/a_T) = A_P \cdot t^{-m} \prod_i \left(1 + \frac{t}{\tau_i}\right)^{\alpha_i} \tag{2}$$

In this description the A_P and m coefficients gives the global decreasing trend while each couple α_i, τ_i gives a located kick turn in the master curve at the specific time τ_i.

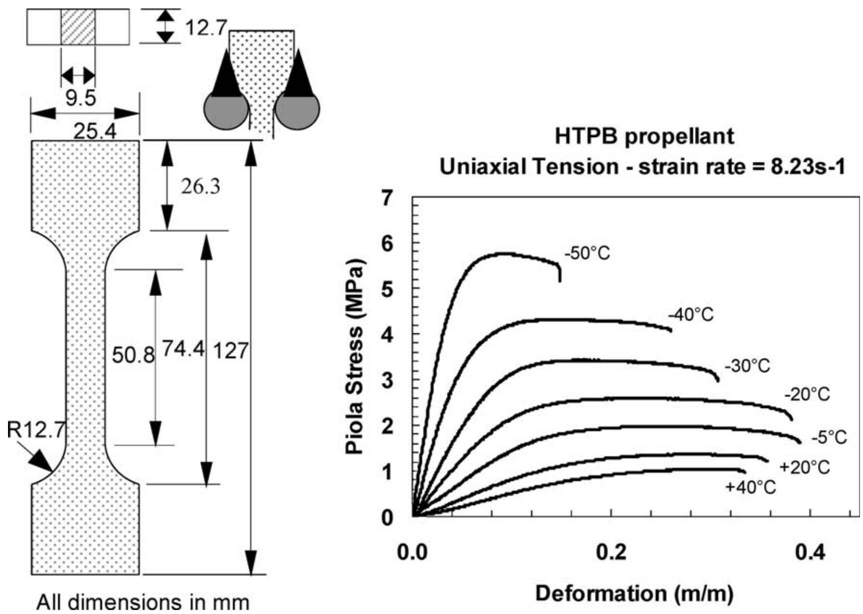

Fig. 3. JANNAF standard and typical uniaxial tensile tests results.

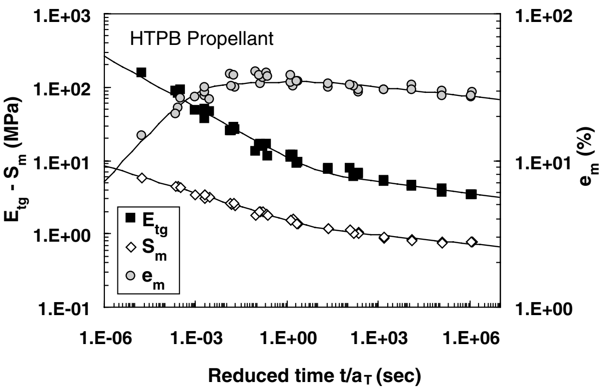

Fig. 4. Master curves of the conventional tensile properties.

It should be reminded from these typical results, the following features:

1. Tangent modulus and maximum stress increase proportionally as the strain rate increases or, by equivalence, as the temperature decreases. It can be shown a correlation between these two properties which are manifestations of the crosslinking density.
2. Both the fracture strain and the strain at maximum stress follow a non-monotonic evolution according to the failure envelope concept as introduced by Smith (1960) for elastomer materials.
3. As a consequence, the non-linear response depends strongly on the experimental conditions of time and temperature.
4. The non-linear behavior is related to the dewetting process which is also known to be time and temperature dependent.

According to these experimental evidences, conventional linear or non-linear viscoelastic description (instantaneous hyperelastic response each coefficient of which relaxes according to a single time kinetics) fails to reproduce the observed behavior. In these models, the time dependence allows to fit the apparent rigidity increase while the instantaneous hyperelastic response introduces a mean non-linear feature which can however not account for the continuous change in the "breaking point" of the curves due to the strain at maximum stress evolution.

3. Results and discussion

3.1. Extension of the superposition principle

3.1.1. Uniaxial tension

Following Schapery (1982), the situation suggests the introduction of a pseudo-strain measure in such a way that the strain at maximum stress varies naturally with the experimental conditions:

$$\varepsilon^* = \int_0^t \varepsilon(t-\tau)\,\mathrm{d}\tau \tag{3}$$

More convincingly than a theoretical discussion assessing the opportunity of this assumption, its consequence on the experimental data treatment shows that the introduction of such a variable allows the superposition of all the non-linear stress–strain responses on a single intrinsic curve independently of the experimental conditions. This treatment suggests to apply a scale factor on the strain axis as well as on the stress axis, this latter being simply the natural consequence of the classical viscoelastic assumption. Fig. 5 shows the superposition obtained by this treatment on the complete set of tensile tests results presented in Fig. 1 which was gathered for temperatures ranging from −50 °C up to +60 °C and tensile rates of 5, 50 and 500 mm/min (40 curves).

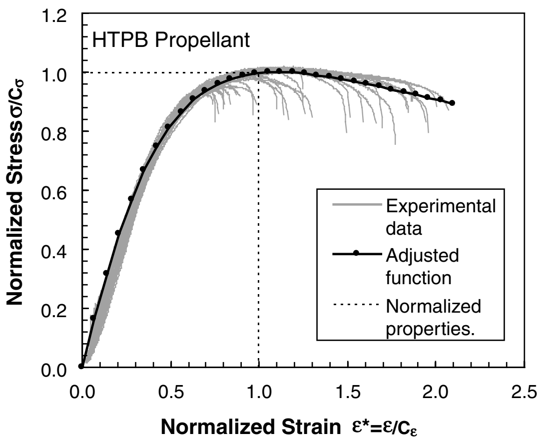

Fig. 5. Superposition of a set of tensile stress–strain response on a unique curve.

Though this superposition is noticeable, this quite spectacular result is just the direct consequence of the time temperature superposition principle applied to the experimental data treatment and extended by the Schapery's pseudo-strain concept. The additional information which may be derived from this result is the existence of a unique non-linear material response in the normalized strain–stress plane. This unique non-linear response may then be understood as a material property by itself. The normalization factors which were introduced to obtain the superposition are of course viscoelastic properties that can be correlated to the conventional tensile properties as presented in Fig. 6. The $C_\sigma(t/a_T)$ factor is obviously the inverse of the maximum stress while the $C_\varepsilon(t/a_T)$ factors is proportional to the modulus once the curve has been previously corrected by C_σ.

3.1.2. Volumetric behavior

It should be emphasized that the same normalization factors (in fact C_ε and $1/C_\sigma$) allow the superposition of the entire set of the isothermal volumetric responses as well. Such a superposition is shown for another HTPB propellant in Fig. 7.

At this stage, comments should be made about the physical consequence of the extracted results from the data treatment. Once again, the unique stress and dilatational response of the material in the normalized space suggests that, rid of the viscoelastic effects, the behavior is controlled by the dewetting process and credit should once again go to the fundamental work of Farris (1968) for a thorough description.

3.1.3. Equibiaxial behavior

The main motivation of these developments is the numerical identification process by a least square technique of a phenomenological model available in the ABAQUS code devoted to hyperelastic materials

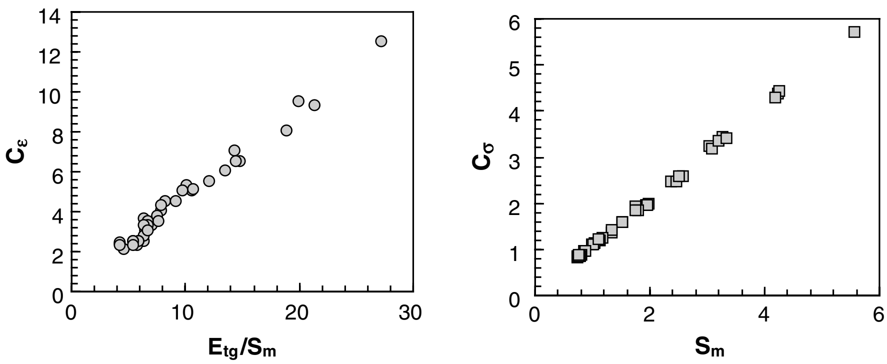

Fig. 6. Correlation of the normalizing factors C_ε and C_σ with the tensile properties.

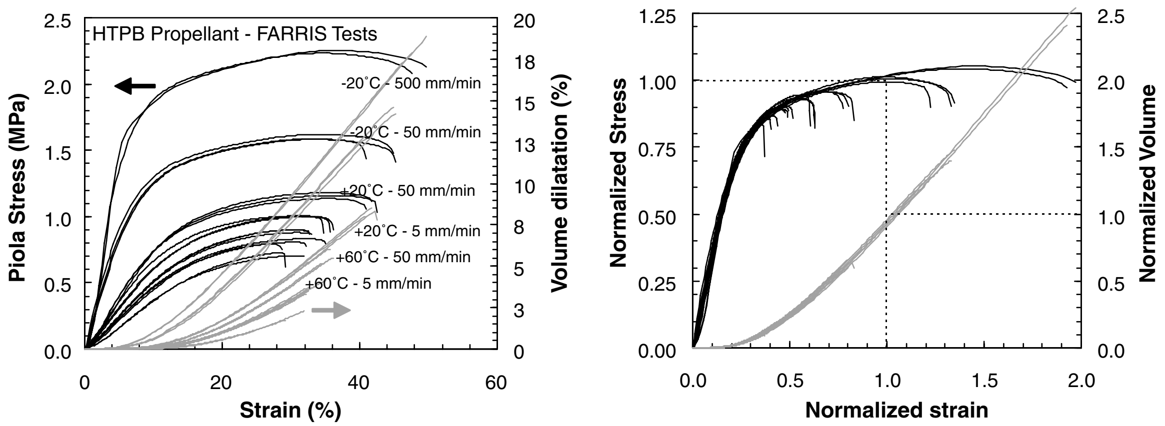

Fig. 7. Superposition of the volumetric responses.

including viscoelastic effects. It is an established fact that this non-linear model requires, in order to insure stability of the solution, a set of experimental data for more than the single uniaxial tension strain field. It is known by the experimentalists of the rubber industry that achievable pure strain fields are very scarce and among these very few, the most informative is the equibiaxial tension test. For these soft and deformable materials, the conventional technique is the inflation of a thin membrane leading to the desired equibiaxial tension state at the pole. Unfortunately, the aggregate structure of solid propellant prohibits this solution and experimental results are gathered using a radial tension original set up. Typical results are presented for an HTPB propellant in Fig. 8.

A long practice of solid propellant mechanical testing have established that for equibiaxial tension and according to the expected theoretical statements, the apparent rigidity of the material response is twice the measured value in uniaxial tension and that more specifically for propellants, the stress is about the same. It is also admitted that the strain at break is divided by two when compared to the uniaxial reference at the same temperature and strain rate. Qualitatively, it is pointed out that the superposition principle is still valid for this particular strain field and that the same intrinsic non-linear response is deduced from the axis normalization process. This result obviously extends the validity domain of the intrinsic curve probably to any multiaxial strain fields and provides a powerful tool to describe the material behavior.

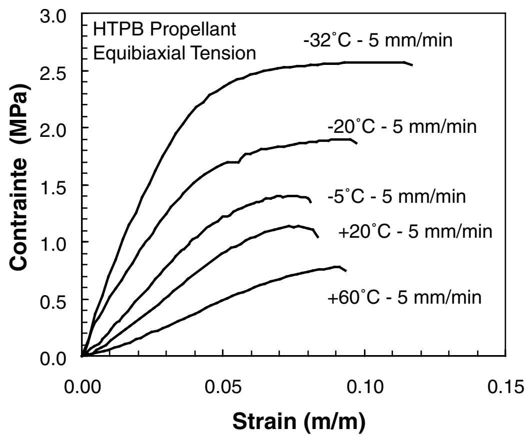

Fig. 8. Typical equibiaxial tension results for an HTPB propellant.

3.1.4. Intermediate conclusions

At this stage of the description, it seems useful to remind and summarize the well established statements.

1. Following Schapery's suggestion, one can easily superpose a set of uniaxial tension results gathered for different strain rates and temperatures by the introduction of two independent normalizing factors respectively on strain and stress axis.
2. The normalizing factors may be drawn as master curves using the conventional shift factors that may be derived from a DMA characterization.
3. This result is just an alternative way to express the time–temperature equivalence principle and the viscoelastic nature of the behavior but the evidence of a unique intrinsic non-linear response, invariable whatever the experimental conditions, states that this non-linear behavior is a material property by itself.
4. It is ascertained that the same scaling factors allow a superposition of the volumetric behavior as well. The intrinsic response then obtained offers a micro-mechanical modeling opportunity which is beyond the scope of this paper but reference to Farris work is recommended to pursue this task.
5. The equibiaxial tension behavior fulfills the superposition requirements and leads to the same intrinsic non-linear response derived from uniaxial tension. It is expected that any multiaxial strain field would lead to the same result.

Together, all these evidences establish the intrinsic non-linear response as a material property which may be understood as an extension of the time–temperature equivalency principle in the non-linear field. This extended principle obviously offers many potential applications both in the materials constitutive models derivation as well as in the experimental data processing techniques. For instance, the propellant mechanical properties scatter has been successfully quantified by the means of an attentive study of the scaling factors. Besides this future potential development, and to illustrate the convenience of the principle, the method is used here to build up a coherent set of material behavior data, cleared of the experimental scatter and representative of the principal feature of the experimental knowledge.

3.2. Material database generation

With the objective of viscoelastic constitutive models identification by numerical processes, the first step of the method consists in fitting a curve to adjust the intrinsic non-linear response. Such a stress–strain relationship, in common use for solid propellants, is (Dubroca, 1982):

$$\sigma = E_{\mathrm{tg}} \cdot \frac{\varepsilon}{a(\varepsilon/e_{\mathrm{m}})^{x} + 1} \tag{4}$$

Once the parameters E_{tg}, e_{m}, a and x are identified and fixed, a set of self coherent material responses for the uniaxial tension field may be generated for any required characteristic time using the kinetics of the scaling factors $C_{\varepsilon}(t/a_{\mathrm{T}})$ and $C_{\sigma}(t/a_{\mathrm{T}})$ in the type of Eq. (2). To provide the equivalent data set for the equibiaxial tension strain field, the same non-linear curve is used but the constants are adjusted to provide twice the value of the rigidity modulus, the same maximum stress and half the value of the strain at maximum stress. To stabilize the viscoelastic numerical identification process and though this information is redundant, a stress relaxation (5% strain) experiment derived from the adjusted kinetics (Eq. (2)) is added to the database. Fig. 9 shows such a database for a typical HTPB propellant in a stress–time plane ranging from 10^{-8} up to 10^{+8} s, which is obviously beyond the achievable domain of the common experimental techniques. It should also be emphasized that, since the adjustment curve process fits the entire superposed set of experiments including the cold temperatures ones where the fracture strain is small, the technique provides a natural extrapolation to higher fracture strains for these curves. This advantage leads to an enhanced numerical stability of the model response in later calculations.

Considering the constraint of the stress analysis of the propellant structures in terms of characteristic times and as long as the assumptions on which the whole approach is built up (time–temperature superposition principle and multiaxial results features) is verified, the proposed method provides a powerful tool to summarize

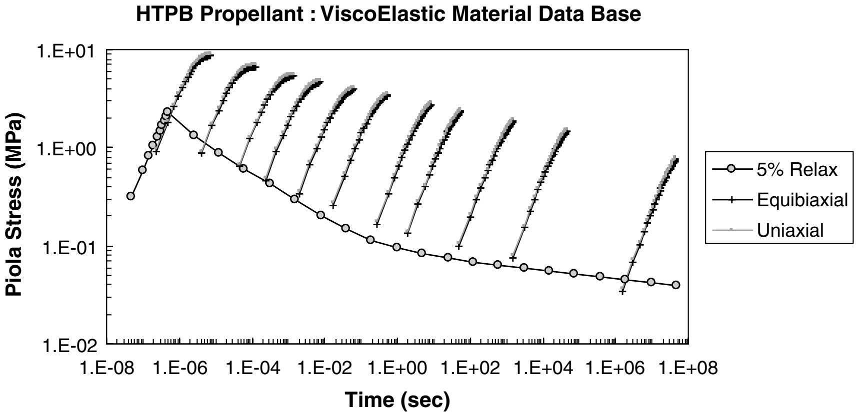

Fig. 9. Material database derived from the unique curve method.

the mechanical behavior knowledge of solid propellants in a coherent database which may input any constitutive model optimization process.

With more or less successful results, the complete process has been unfolded to identify the HyperVisco-Elastic model available in the ABAQUS mechanical structure finite elements analysis software. In a few words, this model assumes an instantaneous hyperelastic response, σ_{inst}, in which all constants are varying with time according to a single viscoelastic kinetics, $R(t)$, adjusted by a Prony series:

$$\sigma(t) = \sigma_{\text{inst}} + \int_0^t R(t-\tau) \cdot \dot{\sigma}(\tau)\, d\tau \tag{5}$$

One should refer to the ABAQUS theory manual (ABAQUS, 1997) to get a more precise description of the model but it obviously appears that by its construction assumptions, such a model is inefficient to reproduce the expected evolution of the kick turn in the solid propellant experimental curves with the experimental conditions. Indeed, such a model leads to a constant non-linear behavior in which only the apparent rigidity is affected by the viscoelastic effects and, as a consequence, the maximum stress is reached for a determined value of the strain. If such a behavior may be expected for a great number of natural or synthetic particle filled elastomers, the complex nature of the solid propellant structure and the diverse sources of the internal energy dissipation sort this very particular material far beyond these "simple" behavior and by no way one can expect to fit the observed response by a single viscoelastic kinetics. Aware of this limitation the fitting procedure leads to the typical result of Fig. 10 which compares the adjusted model to the database in uniaxial tension.

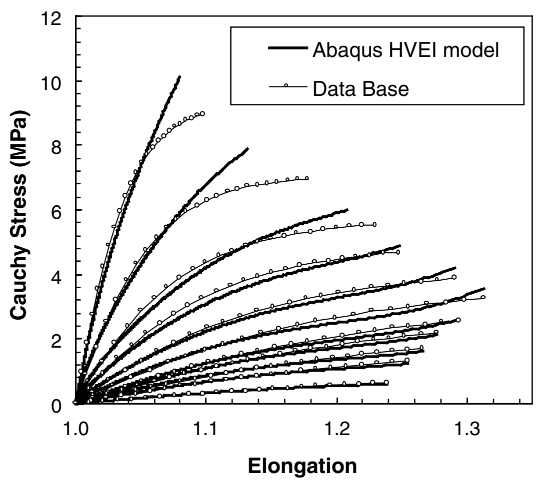

Fig. 10. HyperViscoElastic Abaqus Model adjustment to the database.

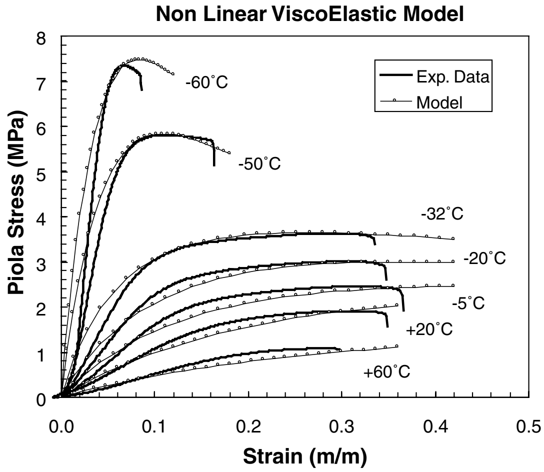

Fig. 11. Pseudo-strain model adjustment.

The presented results suggest that to the classical rigidity viscoelastic dependence should be added a second viscoelastic process in the sense of the Schapery's pseudo-strain which, by an indirect way, affects the apparent strain. Without going into the details, the actual model developments include this strain definition but requires a specific treatment in the FE calculation code (User defined Material behaviour routine UMAT). As a preliminary result, Fig. 11 shows the adjustment of such a model to a set of uniaxial tensile experiments ranging from −50 °C to +60 °C at a constant rate of 8.23 s^{-1}.

The proposed model considers a non-linear description of the stress response as Eq. (5) in which the strain measure is replaced by a multiaxial equivalent strain, ε^*, derived from a von Mises like definition as suggested by Farris and later workers (Özüpeck and Becker, 1997):

$$I_\gamma = \sqrt{I_1^2 - 6 \cdot I_2} \tag{6}$$

The kick turn in the curves is obtained by a slight modification of the conventional convolution product to introduce the normalization factor C_ε:

$$\sigma(t) = \int_0^t E(t-\tau)\frac{\partial}{\partial\varepsilon}[g(\varepsilon^*)]\,\mathrm{d}t \tag{7}$$

At this stage, the model achieves a satisfactory fit on strain–stress curves but is still incompressible and pressure independent. It should be quoted that this class of models requires a double convolution product, the numerical treatment of which is not available in commercial codes.

3.3. Generalization to the elastomer materials class

The presented approach is devoted to solid propellants but curiosity leads to check a potential application to other materials of the filled elastomers class. The experimental data concern a SBR formulation provided by LRCCP (LRCCP stands for Laboratoire de Recherche et de Contrôle du Caoutchoucs et des Plastiques—Vitry FRANCE). Results are available for uniaxial tension (UT) at different constant strain rates and temperature using H3 standard samples. Another set of data concerns a Natural Rubber material and consists in uniaxial tension (UT) but with clamped bars samples, equibiaxial tension (ET) and pure shear (PS) strain fields. For this latter data set, results are restricted to ambient temperature and a single rate. All these data are also courtesy of LRCCP and the test procedure is a point by point measurement after a 10 min relaxation period. Figs. 12 and 13 show the superposition of isothermal uniaxial results while Fig. 14 shows the multiaxial responses superposition.

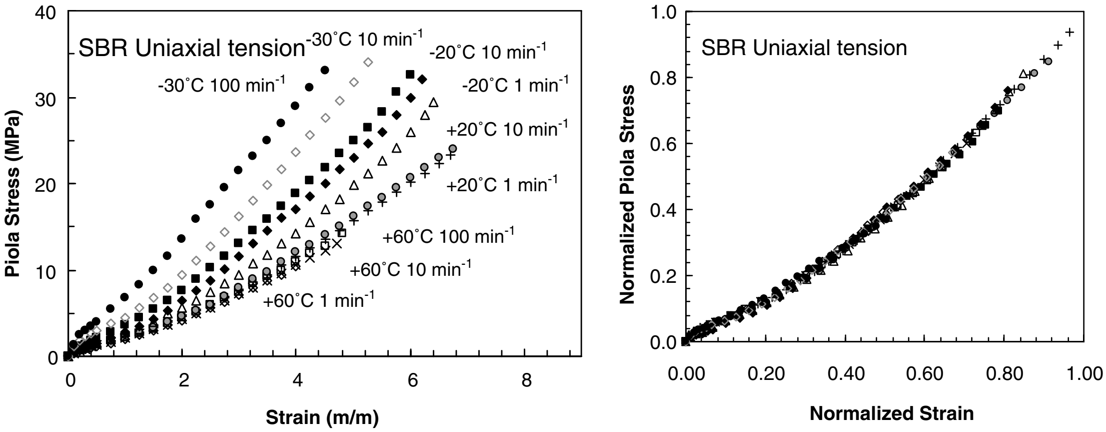

Fig. 12. Isothermal uniaxial tension tests superposition.

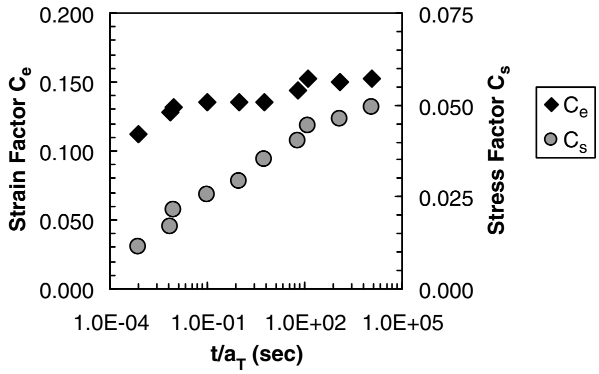

Fig. 13. Master curves of the normalization factors of SBR.

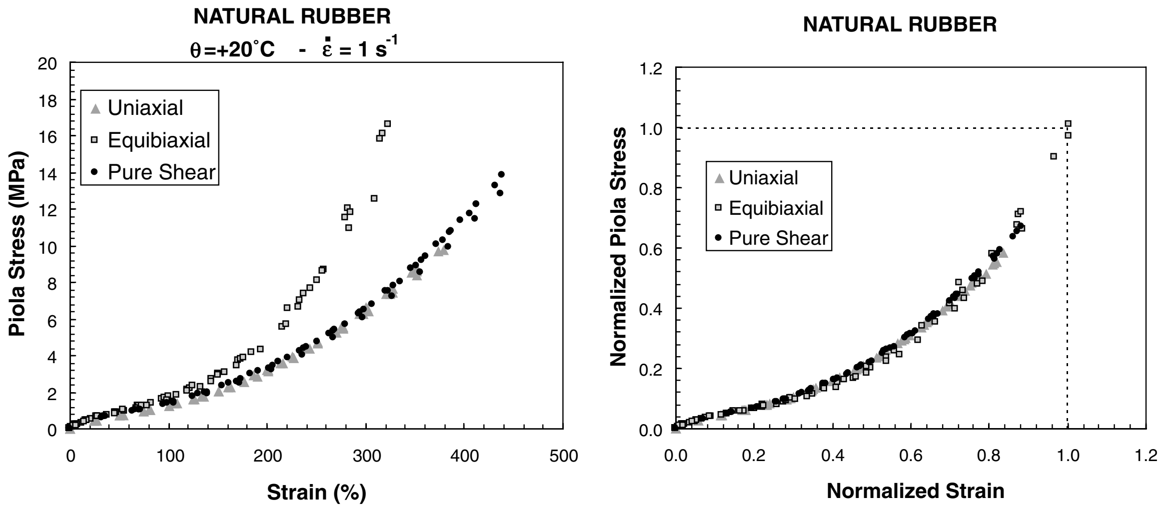

Fig. 14. Multiaxial stress responses superposition of SBR.

The results for these two materials confer an extended generality of the superposition principle which may be expected to be valid for a wide class of elastomers. We do not doubt that a great number of elastomer materials may lead to the same results as long as the time–temperature sensitivity is due to viscoelasticity. However, restriction is expected for materials in which structure modification takes place when the experimental conditions are varied such as crystallization sensitive rubbers (for SBR results presented, crystallization indeed occurs beneath -30 °C and limits the validity domain to this temperature).

4. Conclusions

Following Schapery's pseudo-strain concept, an original method is developed which allows the superposition of a set of uniaxial tensile tests responses measured in a wide domain of strain rates and temperatures. The superposition process involves normalization factors applied independently on the strain and stress axis. These factors are found to be viscoelastic in nature and related to the conventional mechanical properties. The evidence of a superposition capability is an alternative manifestation of the well known time–temperature equivalence principle but the existence of a unique intrinsic response in the normalized stress–strain plane extends the validity of the principle to the field of non-linear viscoelastic behaviors.

The superposition principle validity is experimentally verified both for the volumetric and the biaxial behavior without introducing any additional normalization factor. It makes no doubt that the potential application fields of this principle are numerous but in this paper, emphasis is made on the generation of a coherent material database with the intended purpose to enter a numerical identification process of viscoelastic available models. However, attention should be paid to the physical consequences of the existence of a non-linear intrinsic response and obviously this result should address the micro-mechanical process of debonding by which these materials progressively damage before fracture.

Using the proposed principle, a material coherent database is generated in which the principal features of the mechanical behavior are reproduced but cleared of the experimental scatter. The method offers the advantage of a great coherence, especially concerning the expected modulus ratio between uniaxial and equibiaxial tension, the underlying existence of a single time kinetics for all properties and finally allows for a slight extrapolation of the results beyond the fracture point. With this database, the curve fitting numerical process leads to quite satisfactory results despite the fact that the model assumptions are insufficient to reproduce the characteristic evolution of the kick turn of the curves.

The derivation of a more efficient model requires a theoretical and numerical development which is still undergoing but preliminary results demonstrate all the improvement which may be expected from the introduction of a pseudo-strain variable as suggested by the strain axis coefficient evidence.

Finally, to give an extended generality to the method, the superposition principle is verified for a typical industrial elastomer, namely an SBR rubber.

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